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Observation of Chemical Form of Ions in Aqueous Salt Solutions during Freezing Process by Far-Ultraviolet CTTS Band

Akifumi Ikehata [1], Yusuke Morisawa [2]

[1] National Food Research Institute, NARO, [2] Faculty of Science and Engineering, Kinki University

Summary

Although understanding of chemical states of salts and ions is significantly important to reveal nature of life and preservation of food, there has been no direct observation method. This research project proposes a spectral approach to direct observation of ions based on the first electronic transition ($\tilde{A} \leftarrow \tilde{X}$) of water and charge transfer to solvent (CTTS) of halogen ions by use of attenuated far-ultraviolet (ATR-FUV) spectroscopy the authors developed. $\tilde{A} \leftarrow \tilde{X}$ band of water shows change in hydrogen bonding, for example the peak wavelengths are observed at 155 nm and 149 nm for liquid water and ice, respectively. CTTS band of iodide ion observed in UV range is known as a good chromophore for direct observation of anions because it obeys Beer's law. However, chloride ion that is our target, shows its CTTS band in the FUV range peaked at 175 nm. The only way to observe this band is ATR-FUV spectroscopy. At first, an ATR accessory was developed for cooling of the sample salt solutions with liquid nitrogen. This accessory realized measurement of ATR-FUV spectra from room temperature to about -35°C. Next, according to the famous phase diagram of brine, we investigated freeze-and-thaw processes of NaCl solutions with different concentrations to demonstrate the usefulness of ATR-FUV spectroscopy. During freezing process, condensation of ions with separation of ice was observed by increase of the intensity of CTTS band of chloride ion. The phase transition to eutectic solid phase was also differentiated by CTTS band. Moreover, it is found that all CTTS spectra of the solutions with different concentrations showed the same feature just above the melting temperature of eutectic -21.1°C. This result indicate that NaCl-water solids melt via solution having eutectic concentration i.e. 23.31 wt% without depending on the initial concentrations. The usefulness of ATR-FUV spectroscopy for quantification and observation of states halogen ions of was evaluated.